

Article

Exploring the Presence of Five Rare Earth Elements in Vineyard Soils on Different Lithologies: Campo de Calatrava, Spain

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Abstract: The aim of the work described here was to understand the pedogeochemical signature of five rare earth elements (REEs; Ce, Nd, La, Y, and Sc) in vineyard soils in Campo de Calatrava (a unique territory with calcareous, volcanic and metamorphic rocks). The mean contents in surface horizons of Ce, Nd, La, Y, and Sc were 65.7, 32.0, 35.5, 18.8, and 13.9 mg·kg⁻¹, respectively. In subsurface horizons the contents were Ce 62.8, Nd 31.1, La 35.7, Y 17.9, and Sc 14.4 mg·kg⁻¹. The results show that mean contents of REEs in the area under investigation are in the order Ce > Nd > La > Y > Sc. Ce has a very high range, with a value close to 150 mg·kg⁻¹. On the other hand, concentrations of Ce, Nd, Y, and Sc are higher in soils on volcanic material than in soils on nonvolcanic material, while only La values are lower in soils on volcanic rocks. The distributional maps of REEs in surface and subsurface horizons suggest that parent material and pedogenesis such as argillization and calcium carbonate accumulation are more important factors than the use of REE-based fertilizers, except in certain exceptional cases (consistent with a possible specific human impact after continuous fertilization).

Keywords: viticulture; geostatistics; spatial distribution; *Vitis vinifera* L.; REEs; La Mancha



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1. Introduction

Soil is a multicomponent, biogeochemical open system that contains liquids, solids and gases. As an open system the soil exchanges energy and matter with the surrounding biosphere, atmosphere and hydrosphere [1]. In a vertical stratification the soil consists of a series of horizons produced by different processes in which the continual influence of percolating water and living organisms is felt [2].

Spanish soils have a manifestly Mediterranean character over a large proportion of the territory. A significant proportion of these soils support vineyard crops. Spain is the second-largest producer of grapes for wine in Europe and represents 29.6% of Europe's annual wine production [3,4]. Vineyards are considered to be distinctive landmarks in the local economy and rural landscape in La Mancha (Central Spain), which includes the Campo de Calatrava territory—a region in which grapevine cultivation is very common. Indeed, in this region the soil-climate-vine triangle has been suitably combined for several decades. Campo de Calatrava (Figure 1) can be considered as a rural area that has a unique cultural heritage and vineyards have played a key role in the agricultural economy of this region, particularly in the last 2–3 decades. However, this idyllic aspect is now experiencing certain tangential aspects of an ecological nature, such as increased irrigation.

The so-called REEs are a strategic resource that has recently attracted interest in industries such as automotive, electronics, petrochemicals and environmental energy [5]. These elements are necessary in aerospace engineering, consumer electronics, lasers, fuels

additives, televisions, satellites, energy storage, air bags, wind turbines and, in particular, in different applications in the defense industry [6–8].

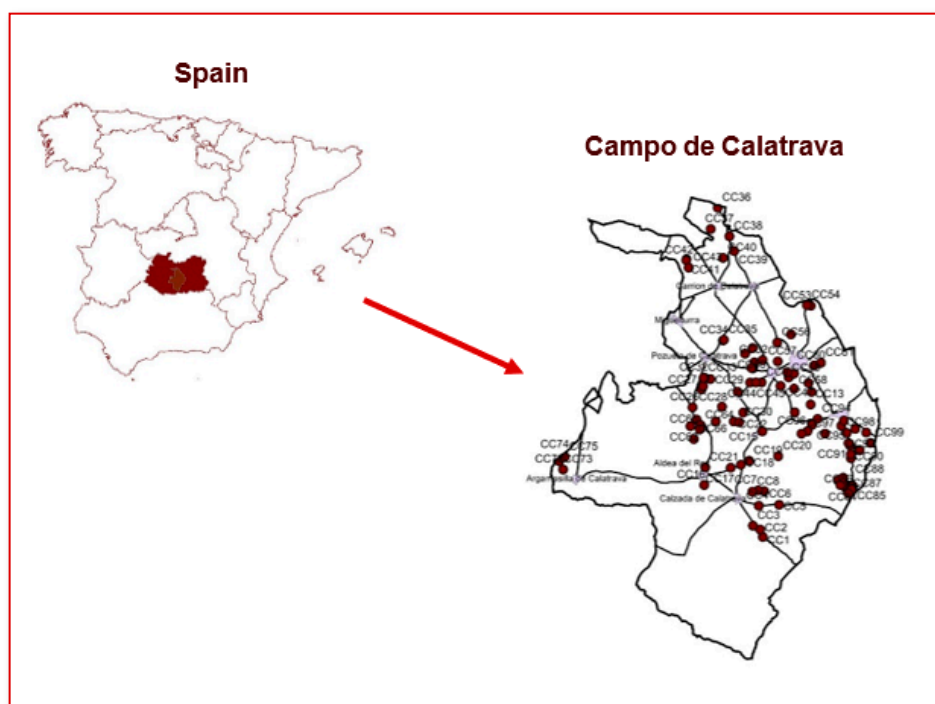


Figure 1. Location and map of the study area. Locations of sampling points (87 soil profiles).

It has been noted [9–11] that the extraction and production of these emerging contaminants can have a significant environmental impact, with the consequent ecological effects. Therefore, there is some social alarm surrounding REEs and this seems to be happening in the studied area. Indeed, today there is a conflicting situation caused by the presence of REEs at higher levels than the background values—a situation that is causing a true social dispute because there is a possibility that a mine will be opened to extract these elements. As a consequence, Campo de Calatrava is an area that is affected by relevant environmental pressures related to REEs.

There is controversy regarding the health benefits vs. toxic effects of REEs [12]. Therefore, they have been cited from protective health effect [13] to toxicological health impacts [14–16], although the main focus of attention is on environmental issues associated with the production, processing, and utilization of REE. In particular, there are many more environmental issues associated with the mining, isolation or recycling of REEs [12]. In fact, the available literature on REE-associated toxicity is confined to a few REEs, mostly Ce, La, and Gd.

Rare earths, as with other trace elements, could provide a powerful tool to ascertain the provenance of a wine [17–19]. The main line of current research is focused on the differences proportions of the trace elements measured in the soil–plant–wine system or the different proportion of their isotopes (mainly $\text{Sr}^{86}/\text{Sr}^{87}$) [20].

The distinguishing feature of Campo de Calatrava, in addition to its history, is the almost unique presence of volcanic materials in mainland Spain. It is worth considering how important it is when materials of a volcanic nature come together, albeit in some cases imbricated with other materials of a carbonatic nature.

Based on the information outlined above, and given the lack of previous studies on the presence of REEs in vineyard soils of Campo de Calatrava, the purpose of the present work was (1) to determine the elemental concentrations of five REEs (Ce, Nd, La, Y, and Sc) in surface and subsurface horizons of vineyard soils, identifying the sources, (2) to

compare the values of REEs between soils on volcanic materials versus soils on nonvolcanic materials and (3) to evaluate the spatial distribution of these elements.

2. Materials and Methods

2.1. Study Area

Geologically, the study area is located in the so-called 'Campo de Calatrava', which is formed by three fundamental morphostructural elements: the paleozoic base, the tertiary sedimentary basins and the recent volcanism. Lithologically, rocks of precambrian age (schists and shales) in a discordant way of detrital nature, fundamentally quartzite, are the predominant rocks [21]. There are numerous modeling features of notable interest, with the accumulation of falling pyroclasts, such as ash, lapilli, slags, and bombs [22].

Campo de Calatrava is a territory characterized by a temperate Mediterranean-type climate, which is conditioned by altitude and isolation from oceanic influences. The striking characteristic of this area is its strong thermal contrasts, with cold winters and hot summers. The summer is warm, with a daily mean air temperature of around 22 °C, whereas the winter is cold, with a mean temperature of around 5 °C. The average annual rainfall is in the range 400–450 mm and this has an irregular behavior year-on-year. Evapotranspiration is high, with a value of over 700 mm/year, and this is concentrated in the summer months.

The vegetation in the Campo de Calatrava belongs to sclerophyllous and subsclerophilic forests with persistent leaves adapted to an environment with prolonged summer drought. In this respect it is worth highlighting the oak *Quercus ilex subsp. ballota*, the gall oak *Quercus faginea subsp. broteroi* and, with a very limited distribution, the *Quercus suber*. Over time this vegetation has led to a target field based on crops such as vineyards, olives and cereals, along with a variety of horticultural crops. Regarding the vineyard, the Airén variety is the native grape in this area but other cultivars include Tempranillo, Garnacha, Merlot, Cavernet Sauvignon and Boval.

The soils of Campo de Calatrava have been described and classified in [23]. According to this reference, the main soil orders are Alfisols, Inceptisols and Entisols [24]. Mollisols and Ultisols appear to a lesser extent and these orders correspond to Luvisols, Calcisols, Cambisols, Leptosols and Regosols, along with lower amounts of Acrisols and Kastanozems [25]. The presence of calcic or petrocalcic horizons is very common. Entisols usually occupy the crest and mid slopes of the landscapes (mainly paleozoic or volcanic rocks) [23]. The macromorphological features of soil profiles in the studied area show mainly a sequence of horizons Ap-Bt-Ckm, Ap-Bt-Ck, Ap-Bw-Bkm, Ap-Bw-Ck, Ap-Ckm, or simply Ap-Bw-C-R, Ap-C-R or Ah-R type. It is very common to find soils with a high proportion of quartz gravel or petroclastic fragments.

2.2. Sampling

The soil samples (141 in total), which corresponded to 87 soil profiles, were collected from July 2019 to February 2020 in the study area gradually, profile by profile; two subsamples (two replicates) were taken and analyzed from each soil horizon (Figure 1). The coordinates of the sampling locations were obtained using a global positioning system (GPS). These coordinates were used to plot the sample locations to obtain the distribution maps of the elements.

The collected samples were transferred into zip-lock bags and sealed in the field. The samples were air-dried and sieved through a 2-mm sieve to separate the coarse fraction. The fine fraction was homogenized, ground in a planetary mill (zirconium oxide grinding bowl) and passed through a 200- μ m sieve. The coarse fraction was discarded.

The 141 soil samples were analyzed for the five REEs elements. The pearls of soil samples were analyzed by X-ray fluorescence using a Philips PW 2404 spectrophotometer with a maximum power of 4 kW (set of crystal analyzers for LiF220, LiF200, Ge, PET and PX1, flow detector and twinkle detector). Quality control was achieved by duplicate analysis of certified soil reference materials (NIST 2710 and CRM 039). The limits of detection were: La 2.34, Nd 3.59, Ce 1.33, Y 0.31 and Sc 1.79 (mg·kg⁻¹).

2.3. Statistical and Geostatistical Analysis

Statistical analysis of the data was carried out using Microsoft Office Excel 2013 and the software Statistical Package for Social Science (SPSS 19.0 for Windows, SPSS Inc., Chicago, IL, U.S.A., under licenses for the University of Castilla-La Mancha, Spain). For geostatistical interpolations, inverse distance weighting (IDW) was used to predict spatial variability maps: a value for any unmeasured location and to present the concentration of a particular element as accurately as possible.

3. Results and Discussion

3.1. General Characteristics of the Soils of Campo de Calatrava

Depending on the geomorphological units (alluvial terraces, detritic glacia surfaces, cones, structural surfaces, etc.) several pedogenetic processes can act. The main pedogenetic processes that affected the soil formation in Campo de Calatrava were the incorporation of organic matter (with intense mineralization), moderate to strong leaching of carbonates, weathering of some minerals, clay illuviation and rubification [23].

In the study carried out on the soils of Campo de Calatrava [23] it was found that soil pH is slightly basic to neutral and only in selected cases was it slightly acidic. The organic carbon content was very low (1–2%, rarely exceeding 3%). Base saturation is usually 100% and only in a few cases was it close to 50%. In general, the soils are low in P and N but are reasonably high in K. The soils have a moderate water-holding capacity with a rapid release of soil moisture at low tensions. The result of the textural analysis indicated that the dominant soil texture is loam, clay loam, silty clay loam and clay. The electrical conductivity is normally below 1 and only rarely exceeds this value.

Based on the information provided above, the soils of Campo de Calatrava dedicated to vine cultivation can be considered as beneficial due to their nutritional quality and they are suitable to produce quality grapes. In contrast, it was highlighted, as on numerous occasions, that there is some iron deficiency caused by an excess of calcium carbonate and, more specifically, of active limestone. The soils are also deficient in phosphorus and nitrogen, although this problem is overcome by moderate fertilization.

3.2. REE Contents

The REE contents of the vineyard soils are presented in Table 1. The concentrations are calculated to express values for oven-dry weights of the soils. It can be seen that the elements are generally present at low concentrations. The mean contents and their ranges (in brackets) in surface horizons of soils developed in Campo de Calatrava are ($\text{mg}\cdot\text{kg}^{-1}$): Ce 65.7 (145.5), Nd 32.0 (68.1), La 35.5 (74.5), Y 18.8 (21.2) and Sc 13.9 (14.1). In the subsurface horizons of the same soils the values are ($\text{mg}\cdot\text{kg}^{-1}$): Ce 62.8 (149.9), Nd 31.1 (69.4), La 35.7 (82.3), Y 17.9 (24.8), and Sc 14.4 (21.2). Thus, the values for both horizons are very similar and the slight differences between them are believed to be caused by the different soil processes (decarbonation, argillization and rubefaction).

Cerium (Ce) is a rare element that is found in trace quantities in the majority of soils and geological materials. The contents of this metal are generally similar to those of Cu and Zn. In the case reported here the Ce concentrations varied widely and ranged from high to moderate in both horizons (mean values of $65.7 \text{ mg}\cdot\text{kg}^{-1}$ in topsoil and $62.8 \text{ mg}\cdot\text{kg}^{-1}$ in subsoil). The highest Ce content was $165.2 \text{ mg}\cdot\text{kg}^{-1}$ and the lowest was $6.1 \text{ mg}\cdot\text{kg}^{-1}$. These results are consistent with the trend that characterizes the contents in the earth's crust. In 1959 Vinogradov [26] reported Ce values of $60 \text{ mg}\cdot\text{kg}^{-1}$. The high contents observed in some cases are probably linked to human activity.

Table 1. Mean contents ($\text{mg}\cdot\text{kg}^{-1}$) and other statistical data for REEs elements in vineyard soils of Campo de Calatrava. N = number of samples.

	N	Range	Surface Horizons		Mean	Stand. Dev.
			Min	Max		
Sc	75	14.1	9.1	23.2	13.9	12.4
Y	75	21.2	10.5	31.7	18.8	4.3
La	75	74.5	9.5	84.0	35.5	14.1
Ce	75	145.5	19.7	165.2	65.7	26.3
Nd	75	68.1	10.2	78.3	32.0	12.0
	N	Range	Subsurface Horizons		Mean	Stand. Dev.
			Min.	Max.		
Sc	66	21.2	4.8	26.0	14.4	4.4
Y	66	24.8	5.5	30.3	17.9	5.8
La	66	82.3	3.2	85.5	35.7	18.0
Ce	66	149.9	6.1	156.0	62.8	31.2
Nd	66	69.4	5.4	74.8	31.0	14.4

The neodymium (Nd) content had a similar range in both horizons (mean value of $32.0 \text{ mg}\cdot\text{kg}^{-1}$ in topsoil and $31.0 \text{ mg}\cdot\text{kg}^{-1}$ in subsoil) with a standard deviation of between 12 and 14. The highest Nd content was $78.3 \text{ mg}\cdot\text{kg}^{-1}$ and the lowest was $5.4 \text{ mg}\cdot\text{kg}^{-1}$. Therefore, in general terms, the soils in the study area have normal Nd values, i.e., similar to those found in other countries [27,28]. Indeed, a worldwide average value for Nd of $8 \text{ mg}\cdot\text{kg}^{-1}$ has been reported [26].

The lanthanum (La) contents are normal (mean of around $35 \text{ mg}\cdot\text{kg}^{-1}$) but in some cases they are high ($85.5 \text{ mg}\cdot\text{kg}^{-1}$), in which case the soils could be polluted. The highest La content was $78.3 \text{ mg}\cdot\text{kg}^{-1}$ (surface horizon) and the lowest was $5.4 \text{ mg}\cdot\text{kg}^{-1}$ (subsurface horizon). The standard deviations in the two horizons are similar (14.1 vs. 18.0). Tyler [29] reported La values of $44 \text{ mg}\cdot\text{kg}^{-1}$ in Chinese soils and between 5.5 and $33.2 \text{ mg}\cdot\text{kg}^{-1}$ in Swedish soils. In Japan [30] values of $18 \text{ mg}\cdot\text{kg}^{-1}$ were obtained. Tyopine [31] reported mean contents for La of 20.68–32.31 $\text{mg}\cdot\text{kg}^{-1}$, while a value of $39 \text{ mg}\cdot\text{kg}^{-1}$ has also been reported [26].

Regarding yttrium (Y) contents, the average is characterized by normal to moderately low values (between 18.8 for topsoil and $17.9 \text{ mg}\cdot\text{kg}^{-1}$ for subsoil). The highest Y content was $31.7 \text{ mg}\cdot\text{kg}^{-1}$ and the lowest was $5.5 \text{ mg}\cdot\text{kg}^{-1}$. The standard deviation was around 5. Tyler [29] reported a Y value in soils in China of $22 \text{ mg}\cdot\text{kg}^{-1}$ and Zang [32] found a value of $27 \text{ mg}\cdot\text{kg}^{-1}$ in North Vietnam.

With respect to scandium (Sc), the mean concentrations were 13.9 and $14.4 \text{ mg}\cdot\text{kg}^{-1}$ in surface and subsurface soils, respectively, with a high standard deviation found in surface horizons (12.8). The highest Sc content was $26.0 \text{ mg}\cdot\text{kg}^{-1}$ and the lowest was $4.8 \text{ mg}\cdot\text{kg}^{-1}$. These median values are similar to the median values worldwide [26–36]. Evidence for pollution was not found in the studied area. In general, all of the REEs studied had median values for topsoil and subsoil of the same order of magnitude for Castilla-La Mancha [37,38]. Median values for some REE concentrations are slightly higher when compared to the median for some worldwide regions, but they are lower than the averages for other regions. In Table 2 it can be observed that all elements show significant correlation at the 0.01 level.

3.3. Comparison of Values between Soils on Volcanic Materials versus Soils on Nonvolcanic Materials

The descriptive statistics for the individual REEs in volcanic soils are listed in Table 3 along with those for soils developed on materials of nonvolcanic nature (generally carbonatic). Comparison of the mean concentrations of REEs in the soils on volcanic rocks versus nonvolcanic rocks reveals that the former soils are moderately enriched in REEs relative to the latter.

Table 2. Correlation matrix of elements.

Surface Horizon Correlation						
	Y	La	Ce	Th	Nd	Sc
Y	1					
La	0.835 **	1				
Ce	0.884 **	0.973 **	1			
Th	0.811 **	0.705 **	0.730 **	1		
Nd	0.868 **	0.970 **	0.985 **	0.693 **	1	
Sc	0.634 **	0.638 **	0.622 **	0.349 **	0.667 **	1

Subsurface Horizon Correlation						
	Y	La	Ce	Th	Nd	Sc
Y	1					
La	0.853 **	1				
Ce	0.904 **	0.961 **	1			
Th	0.854 **	0.788 **	0.786 **	1		
Nd	0.889 **	0.970 **	0.984 **	0.785 **	1	
Sc	0.690 **	0.755 **	0.731 **	0.670 **	0.778 **	1

** The correlation is significant at the 0.01 level (bilateral).

Table 3. Descriptive statistical data for rare earth elements separated between soils on volcanic rocks and soils on nonvolcanic rocks in Campo de Calatrava.

Soils on Volcanic Rocks						
Surface Horizons						
	N	Range	Min	Max	Mean	Stand. Dev.
Sc	29	11.8	11.4	23.2	15.5	3.6
Y	29	15.7	16.0	31.7	21.9	4.3
La	29	59.3	24.7	84.0	46.9	14.6
Ce	29	119.8	45.4	165.2	102.4	25.4
Nd	29	59.2	19.1	78.3	41.4	12.3

Soils on Volcanic Rocks						
Subsurface Horizons						
	N	Range	Min	Max	Mean	Stand. Dev.
Sc	26	14.6	11.4	26.0	17.7	3.6
Y	26	15.5	14.8	30.3	22.4	4.3
La	26	64.8	20.7	85.5	51.7	14.6
Ce	26	114.1	41.9	156.0	91.4	27.9
Nd	26	53.2	21.6	74.8	44.5	12.3

Soils on Nonvolcanic Rocks						
Surface Horizons						
	N	Range	Min	Max	Mean	Stand. Dev.
Sc	46	9.0	9.1	18.1	12.9	1.9
Y	46	13.9	10.5	24.4	16.8	2.9
La	46	45.2	9.5	54.7	28.3	9.8
Ce	46	76.2	19.7	95.9	52.6	16.8
Nd	46	38.8	10.2	49.0	26.1	7.7

Soils on Nonvolcanic Rocks						
Subsurface Horizons						
	N	Range	Min	Max	Mean	Stand. Dev.
Sc	40	17.6	4.8	22.4	12.6	3.9
Y	40	19.9	5.5	25.4	15.3	5.1
La	40	52.9	3.2	56.1	26.7	14.1
Ce	40	97.5	6.1	103.6	47.4	24.2
Nd	40	42.7	5.4	48.1	23.7	11.0

REE placers, such as those derived from volcanic activity, are rare [39]. Rare earth element concentrations in Campo de Calatrava are slightly higher than the mean REE values of common sedimentary rocks of the same zone; however, the values are well within the concentration ranges of soils of worldwide. Concentrations of Ce, Nd, Y, and Sc are higher in soils on volcanic material than in soils on nonvolcanic material, while only La values are lower in soils on volcanic rocks. Thus, the depletion of REEs is observed in the transition from volcanic to nonvolcanic soils. These distinctive REE patterns between soils on volcanic and nonvolcanic materials could probably provide a characteristic fingerprint for Campo de Calatrava.

3.4. Spatial Distribution

It is evident that the REE maps are locally noisy (Figure 2). Cerium shows a clear distribution in both types of horizons, although there are moderate differences between the two and a clear dispersion is also observed. However, higher surface contents were detected and the values that show the dispersion are not consistent. With regard to Nd, the location maps are reasonably similar between the two horizons, while a moderate dispersion is detected, especially in the subsurface, where medium to high values predominate. In the case of lanthanum, the distribution maps are relatively similar, with medium to high values prevailing, although higher contents are observed in the surface horizon. Furthermore, a clear dispersion is detected but this is not consistent between the two horizons. As far as Y is concerned, comparison of the two maps shows their similarity, with a punctual dispersion that is more marked in the subsurface horizon, with medium to high values predominating. The case of Sc shows fair similarity between the two horizons, with a rather punctual dispersion, especially in the subsurface; medium to low values predominate.

REEs occur naturally as components of minerals in soil. The factors that influence the presence of trace elements such as REEs in soils have been discussed in numerous reports [36]. Firstly, it was found that the REE contents decreased depending on the parent material in the order calcaric rocks > volcanic rocks, as also stated in reference [35]. Different soil-forming processes influence the distribution of total contents of REEs, especially the argillization process and calcium carbonate accumulation.

REEs are either inherited from soil parent materials or are introduced during rock weathering or by inputs from human activity. Soil contamination with REEs due to parent materials or point sources do not typically appear to be like those in the area under investigation. The observation of punctual dispersion in one horizon or another suggests a probable effect of agricultural practices such as the application of chemical and organic fertilizers, which are used as a source of nutrients for plants. The repeated use of fertilizers may cause contamination [40,41]. Other authors have reported a significant increase in the concentrations of some REEs in soils under fertilization: for example, it was reported that phosphorus fertilizer production acts as a source of rare earth pollution in the environment [42–44]. Indeed, given the deficiencies in N and P shown by many soils in Campo de Calatrava [23], the application of chemical fertilizers is frequent. Naturally, the dose and frequency of application determine the potential risk of their accumulation.

Compared with the data from the literature, the values obtained for some REEs in Campo de Calatrava are similar to the regional, national and world soil averages. Furthermore, regardless of the anomalous values found, the differences between horizons are probably related in part to the different carbonate contents found, which in turn depend on the variability of the parent materials and the associated soil genetic processes. Calcium carbonate (present in almost all soils) is present at a relatively high level, i.e., close to 60% [23]. These data are consistent with the results reported in reference [5] in the sense that carbonates influence the distribution and migration of REEs. Therefore, with the exception of some scattered samples that present abnormally high values, in general terms the samples contain similar levels of REEs throughout the territory, which suggests a common lithogenic and pedogenetic origin.

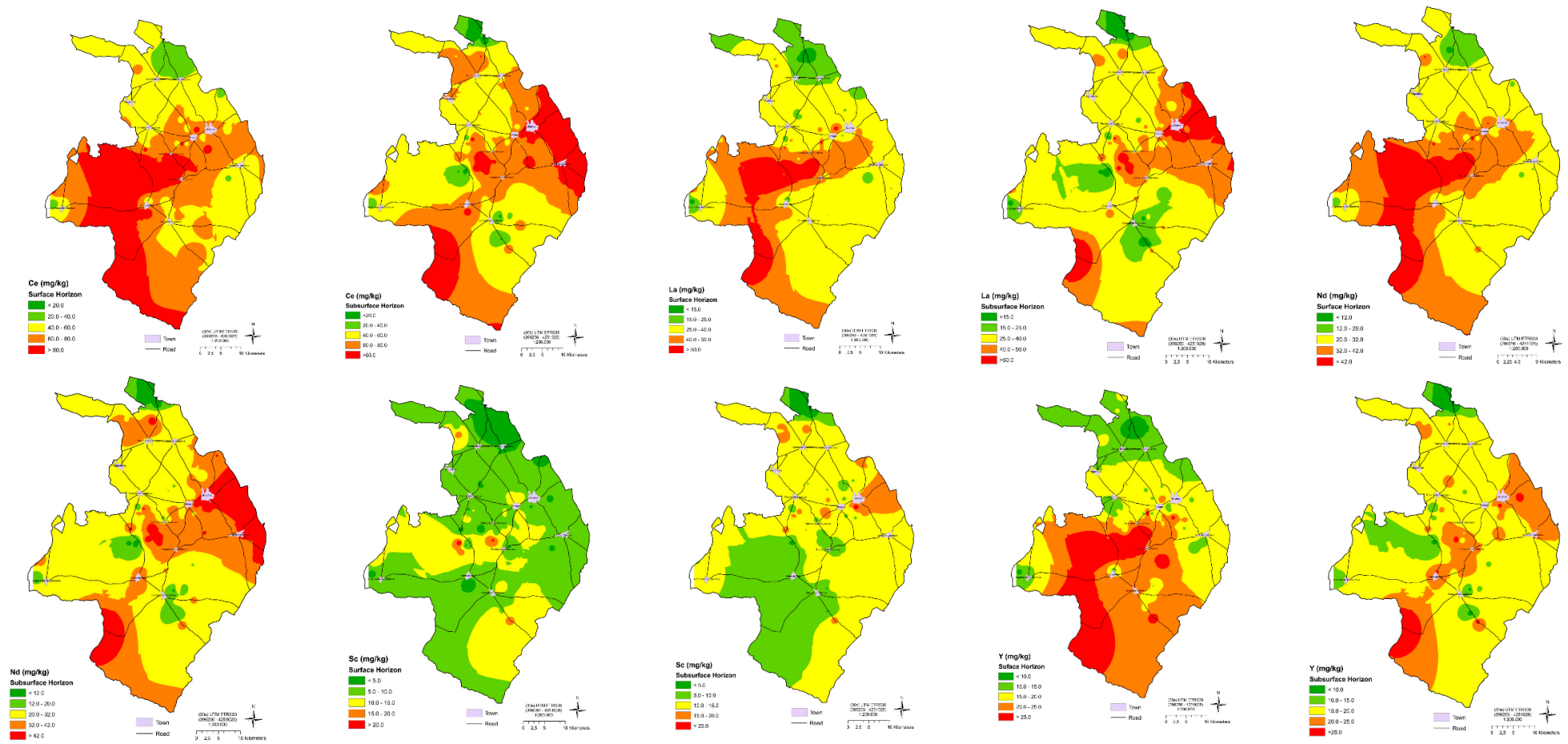


Figure 2. Spatial distribution maps of Ce, Nd, La, Y, and Sc concentrations in surface and subsurface horizons.

REEs are mobile elements during soil formation [45] and the typical weathering profiles of dolomite and limestone were analyzed [33], albeit under different conditions than those reported here. Recently, it was revealed that the greater or lesser mobility of these elements depends on whether they are heavy or light elements and also on whether they are in the surface or subsurface horizons [46]. These findings are consistent with the values for surface and subsurface horizons in the study area (both horizons are very similar values with slight differences between them).

The soils of Campo de Calatrava differ from any mere weathered rock. In the vicinity of the paleozoic or volcanic hills, very old geological formations and long periods of exposure to the elements have given rise to very old soils (probably the oldest in Europe). These soils show an advanced state of weathering along with the formation of red soils. This type of soil has also been produced from carbonate materials on softer topographies. The persistence of the red paleosols, together with more recently formed Cambisols, Leptosols and Regosols, suggests that soil diversification with time was more a process of adding new varieties of soils than replacing pre-existing ones, as previously stated [33].

Some soils showed abundant clay coatings developed in red Bt horizons of clay (or clay loam) textural class. All of these red soils developed from different parent rocks, i.e., carbonatic (as limestones) or volcanic (as basalts), and metamorphic materials (schists and shales). In addition, the semiarid climate favors calcium carbonate accumulation [47]; Reeves and Braithwaite [48,49] showed that such accumulations are common in arid and semiarid climates, while they have also been correlated with a warm, seasonally dry climate [33,50,51].

In 1932, Weeks [52] stated that the REEs are very much alike and are closely associated in very complex minerals, which makes these elements extremely difficult to separate. It is, therefore, easy to understand that the content in REEs must be influenced by the lithology, as noted in [29]. The content of lithological materials in REEs is a function of the mineral composition [45]. Similarly, it was reported that the natural contents of soils depend fundamentally on the nature of the starting material in the decreasing order granite > basalt > sandstone [35,53], while soils that originate from igneous rocks, schists and sandstone tend to contain more REEs when compared to those that originate from other materials [27]. In a study conducted by Ramos et al. [53] on carbonate materials, and specifically on Chromic Luvisol from China, the values were (expressed in $\text{mg}\cdot\text{kg}^{-1}$) Ce 114, Nd 48 and La 55.

In addition, the distributional scheme in the study area suggests that parent material and pedogenesis are more important factors than the use of REE-based fertilizers—except in certain exceptional cases.

The soil plays a role in the recycling of chemical elements through the earth. In the future, it is necessary to unveil the ecological and human health risks associated with the widespread use of REEs. Given the pH levels in most of the soils of the Campo de Calatrava, which are basic or moderately basic, the soils provide low mobility that prevents REEs from being removed from the soil. However, further studies involving more soil sample analyses and fractionation techniques are required to confirm these results.

This work constitutes the basis for future studies related to the fingerprint of the wines of this unique area, in the same sense as several investigations [54,55] carried out on the origin of a wine taking into consideration the mineral composition.

4. Conclusions

The pedogeochemical signature of the five REEs studied in vineyard soils of Campo de Calatrava have mean contents of Ce 65.7, Nd 32.0, La 35.5, Y 18.8, and Sc 13.9 (in $\text{mg}\cdot\text{kg}^{-1}$) in the surface horizons, while in subsurface horizons the mean contents are Ce 62.8, Nd 31.1, La 35.7, Y 17.9, and Sc 14.4 ($\text{mg}\cdot\text{kg}^{-1}$). The concentrations of the REEs can be arranged in the following order: Ce > Nd > La > Y > Sc.

Comparison of the levels of individual REEs in volcanic soils with those for soils developed on materials of nonvolcanic nature (generally carbonatic) reveals that the former soils are moderately enriched in REEs relative to the latter.

The distributional maps of REEs suggest that parent material and pedogenesis (such as argillization and calcium carbonate accumulation) are more important factors than the use of REE-based fertilizers, except in certain exceptional cases.

Further investigation should be carried out including data of plant and wine content of the studied elements in order to ascertain the behavior of the geochemical fingerprint in the soil–vine system.

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